

1           **ALKYLATED AROMATIC COMPOSITIONS, ZEOLITE CATALYST**  
2           **COMPOSITIONS AND PROCESSES FOR MAKING THE SAME**

3                           FIELD OF THE INVENTION

4   The present invention is directed to novel alkylated aromatic compositions,  
5   zeolite catalyst compositions and processes for making the same. The  
6   catalyst compositions comprise zeolite Y and mordenite zeolite having a  
7   controlled macropore structure. The present invention is also directed to the  
8   preparation of the catalyst compositions and their use in the preparation of  
9   novel alkylated aromatic compositions. The catalyst compositions of the  
10   present invention exhibit reduced deactivation rates during the alkylation  
11   process, thereby increasing the life of the catalysts.

12                           BACKGROUND OF THE INVENTION

13   It is well known to catalyze the alkylation of aromatics with a variety of Lewis  
14   or Bronsted acid catalysts. Typical commercial catalysts include phosphoric  
15   acid/kieselguhr, aluminum halides, boron trifluoride, antimony chloride,  
16   stannic chloride, zinc chloride, onium poly(hydrogen fluoride), and hydrogen  
17   fluoride. Alkylation with lower molecular weight olefins, such as propylene,  
18   can be carried out in the liquid or vapor phase. For alkylations with higher  
19   olefins, such as C<sub>16</sub> olefins, the alkylations are done in the liquid phase,  
20   usually in the presence of hydrogen fluoride. Alkylation of benzene with  
21   higher olefins is especially difficult, and requires hydrogen fluoride treatment.  
22   However, hydrogen fluoride is not environmentally attractive.

23   The use of the above listed acids is extremely corrosive, thus requiring special  
24   handling and equipment. Also, the use of these acids might involve  
25   environmental problems. Another problem is that the use of these acids can  
26   give less than desirable control on the precise chemical composition of the  
27   product produced. Thus, it is preferable to use a safer, simpler catalyst,

1 preferably in solid state. This simpler process would result in less capital  
2 investment, which would result in a less expensive product.

3 Solid crystalline aluminosilicate zeolite catalysts have been known to be  
4 effective for the alkylation of aromatics with olefins. Zeolitic materials which  
5 are useful as catalysts are usually inorganic crystalline materials that possess  
6 uniform pores with diameters in micropore range that is less than  
7 20 angstroms. Zeolites occur naturally and may also be prepared  
8 synthetically. Synthetic zeolites include, for example, zeolites A, X, Y, L and  
9 omega. It is also possible to generate metaloaluminophosphates and  
10 metalosilicophosphates. Other materials, such as boron, gallium, iron or  
11 germanium, may also be used to replace the aluminum or silicon in the  
12 framework structure.

13 These zeolite catalyst materials are commercially available as fine crystalline  
14 powders for further modification to enhance their catalytic properties for  
15 particular applications. Processes for the further modification to enhance  
16 catalytic properties of the zeolite catalysts are well known in the art, such as  
17 forming the zeolite catalysts into shaped particles, exchanging the cations in  
18 the catalyst matrix, etc.

19 Forming zeolite powders into shaped particles may be accomplished by  
20 forming a gel or paste of the catalyst powder with the addition of a suitable  
21 binder material such as a clay, an inorganic compound, or an organic  
22 compound and then extruding the gel or paste into the desired form. Zeolite  
23 powders may also be formed into particles without the use of a binder.  
24 Typical catalyst particles include extrudates whose cross sections are circular  
25 or embrace a plurality of arcuate lobes extending outwardly from the central  
26 portion of the catalyst particles.

27 One problem with catalyst particles used in fixed bed reactors is catalyst  
28 deactivation. In most hydrocarbon conversion processes, including alkylation,

1 the primary catalyst deactivation is caused by coke formation. This catalyst  
2 deactivation is a serious problem in the use of zeolite catalysts for alkylation  
3 reactions. This deactivation problem is well known in the art and it is well  
4 understood that the deactivation mechanism can involve polymerization of the  
5 olefin into large molecular species that cannot diffuse out of the pores  
6 containing the active sites in the zeolitic material.

7 The use of zeolite catalysts for preparation of alkyl aromatics is typically  
8 conducted by the catalytic alkylation of aromatic hydrocarbons with normal  
9 alpha olefins or branched-chain olefins, and optionally a promotor. The  
10 alkylated aromatic hydrocarbons can be converted into corresponding sulfonic  
11 acids which can be further converted into alkylated aromatic sulfonates.

12 A number of patents have discussed processes for the preparation of zeolite  
13 catalysts and the further shaping and forming of the catalyst particles and  
14 extrudates with and without the use of binders. There are also a number of  
15 patents disclosing the use of zeolite catalysts for alkylation of aromatic  
16 hydrocarbons.

17 U.S. Pat. No. 3,094,383 discloses the preparation of synthetic zeolite  
18 materials which upon hydration yield a sorbent of controlled effective pore  
19 diameter and in which the sorbent and its zeolite precursor are provided  
20 directly in the form of an aggregate.

21 U.S. Pat. No. 3,130,007 discloses the method of preparing sodium zeolite Y  
22 with silica to alumina ratios ranging from greater than 3 to about 3.9.

23 U.S. Pat. No. 3,119,660 discloses a process for making massive bodies or  
24 shapes of crystalline zeolites. The patent also discloses methods for the  
25 identification of the catalyst materials using X-ray powder diffraction patterns  
26 in conjunction with chemical analyses.

1 U.S. Pat. No. 3,288,716 discloses that the high "heavy content" of the  
2 alkylated aromatic product can be controlled during the alkylation step and  
3 has advantages over distilling the alkylated aromatic product to obtain the  
4 desired molecular weight.

5 U.S. Pat. Nos. 3,641,177 and 3,929,672 disclose the technique to remove  
6 sodium or other alkali metal ions from zeolite catalysts. The '177 patent also  
7 discloses that such removal of the sodium or other alkali metal ions activates  
8 the zeolite catalysts for the alkylation of aromatic hydrocarbons with olefins by  
9 liquid phase reaction.

10 U.S. Pat. Nos. 3,764,533, 4,259,193 and 5,112,506 disclose the "heavy  
11 alkylate" content influences neutral sulfonates and overbased sulfonates. In  
12 U.S. Pat. No. 5,112,506, the effect of molecular weight distribution or "heavy  
13 alkylate" is shown to influence the performance of both Neutral and HOB  
14 sulfonates and the di-alkylate content is shown to influence the rust  
15 performance of the corresponding sulfonate in U.S. Pat. No. 3,764,533. In  
16 U.S. Pat. No. 4,259,193, a mono-alkylate sulfonate is preferred. U.S. Pat.  
17 Nos. 3,288,716; 3,764,533; 4,259,193; and 5,112,506 are hereby  
18 incorporated by reference for all purposes.

19 U.S. Pat. No. 3,777,006 discloses the use of nucleating centers for the  
20 crystallization of crystalline aluminosilicate zeolites having a size in excess of  
21 200 microns and characterized by high strength and excellent adsorptive  
22 properties.

23 U.S. Pat. No. 4,185,040 discloses the preparation of highly stable and active  
24 catalysts for the alkylation of aromatic hydrocarbons with C<sub>2</sub>-C<sub>4</sub> olefins. The  
25 catalysts are acidic crystalline aluminosilicate zeolites which exhibit much  
26 improved deactivation rates.

1 U.S. Pat. No. 4,395,372 discloses an alkylation process for alkylating benzene  
2 comprising contacting benzene and lower olefins with a rare earth exchanged  
3 X or Y zeolite catalyst in the presence of sulfur dioxide.

4 U.S. Pat. No. 4,570,027 discloses the use of a low crystallinity, partially  
5 collapsed zeolite catalyst for producing alkylaromatic hydrocarbons. The  
6 alkylation reaction also involves conditioning the catalyst bed with hydrogen  
7 prior to conducting the alkylation reaction.

8 U.S. Pat. Nos. 4,762,813; 4,767,734; 4,879,019 and 5,111,792 disclose the  
9 preparation of a hydrocarbon conversion catalyst using a low silica to alumina  
10 ratio zeolite Y bound into an extrudate and steamed to modify the catalyst.

11 U.S. Pat. No. 4,764,295 discloses a process for making non-foaming  
12 detergent-dispersant lubricating oil additives. The process further involves  
13 carbonation for making the products more basic.

14 U.S. Pat. No. 4,876,408 discloses an alkylation process using an ammonium-  
15 exchanged and steam stabilized zeolite Y catalyst having an increased  
16 selectivity for mono-alkylation. The process involves the presence of at least  
17 one organic compound under conditions such that sufficient amount of  
18 carbonaceous material evenly deposits on the alkylation catalyst to  
19 substantially suppress its alkylation activity.

20 U.S. Pat. No. 4,891,448 discloses a process for alkylation of polycyclic  
21 aromatic compounds in the presence of an acidic mordenite zeolite catalyst  
22 having a silica to alumina molar ratio of at least 15:1 to produce a mixture of  
23 substituted polycyclic aromatic compounds enriched in the para alkylated  
24 isomers.

25 U.S. Pat. No. 4,916,096 discloses use of a zeolite Y catalyst for  
26 hydroprocessing. The zeolite Y catalyst comprises a modified crystalline

1 aluminosilicate zeolite Y, a binder and at least one hydrogenation component  
2 of a Group VI or a Group VIII metal.

3 U.S. Pat. No. 5,004,841 discloses a process for alkylation of polycyclic  
4 aromatic compounds in the presence of an acidic mordenite zeolite catalyst  
5 having a silica to alumina molar ratio of at least 15:1 to produce substituted  
6 polycyclic aromatic compounds enriched in the linear alkylated isomers.

7 U.S. Pat. No. 5,026,941 discloses the use of a zeolite Y catalyst having a  
8 silica to alumina ratio of 15 to 110 for the alkylation of naphthalene or  
9 mono-isopropylnaphthalene.

10 U.S. Pat. No. 5,118,896 discloses an aromatic alkylation process comprising  
11 the steps of contacting a hydrocarbon feed with an alkylating agent under  
12 liquid phase alkylation conditions in the presence of a silica-containing large  
13 macropore, small particle size zeolite catalyst, the catalyst having a pore  
14 volume of about 0.25 to 0.50 cc/g in pores having a radius of 450 angstroms  
15 and a catalyst particle diameter of not more than 1/32 of an inch.

16 U.S. Pat. No. 5,175,135 discloses the use of an acidic mordenite zeolite  
17 catalyst for alkylation of aromatic compounds with an alkylating agent having  
18 from one carbon atom to eight carbon atoms to produce substituted aromatic  
19 compounds enriched in the linear alkylated isomers. The acidic mordenite  
20 catalyst is characterized by its silica to alumina molar ratio, its porosity and a  
21 Symmetry Index.

22 U.S. Pat. No. 5,191,135 discloses the process for making long-chain  
23 alkyl-substituted aromatic compounds from naphthalenes, the process  
24 comprising a zeolite alkylation catalyst in the presence of 0.5 to 3.0 weight  
25 percent water. The presence of water increases the selectivity for making  
26 mono-alkylated products.

1 U.S. Pat. Nos. 5,240,889 and 5,324,877 disclose processes for the  
2 preparation of a catalyst composition having alkylation and/or transalkylation  
3 activity and wherein the catalyst composition contains greater than 3.5 weight  
4 percent water based on the total weight of the catalyst composition and the  
5 aromatic alkylation process using said catalyst composition and olefins  
6 containing 2 carbon atoms to 25 carbon atoms.

7 U.S. Pat. No. 5,198,595 discloses a process for alkylation of benzene or  
8 substituted benzene in the presence of an acidic mordenite zeolite catalyst  
9 having a silica to alumina ratio of at least 160:1 and a Symmetry Index above  
10 about 1.0. A process for the preparation of the catalyst is also disclosed.

11 U.S. Pat. No. 5,243,116 discloses the production of alkylated benzenes by  
12 alkylation and/or transalkylation in the presence of an acidic mordenite zeolite  
13 catalyst having a silica to alumina molar ration of at least 30:1 and a specific  
14 crystalline structure determined by X-ray diffraction.

15 U.S. Pat. No. 5,453,553 discloses a process for the production of linear alkyl  
16 benzenes which process comprises co-feeding a mixture of benzene, linear  
17 olefins and molecular hydrogen in the presence of a zeolite catalyst  
18 containing a transition metal under alkylation condition such that the catalyst  
19 is not deactivated.

20 U.S. Pat. No. 5,506,182 discloses the preparation of a catalyst composition  
21 comprising 10 to 90 percent of a modified zeolite Y catalyst formed from a  
22 modified zeolite Y and 10 to 90 percent binder using slurries of the modified  
23 zeolite Y and the binder to form the catalyst composition having a clear  
24 absorption peak in an IR spectrum of a wavelength of 3602 per centimeter.  
25 The patent also discloses the substitution of iron for the alumina in the  
26 zeolite Y structure.

1 U.S. Pat. No. 5,922,922 discloses a process for isomerizing a normal alpha  
2 olefin in the presence of an acidic catalyst having a one-dimensional pore  
3 system, and then using the isomerized olefin to alkylate aromatic  
4 hydrocarbons in the presence of a second acidic catalyst, which can be  
5 zeolite Y having a silica to alumina ratio of at least 40 to 1.

6 U.S. Pat. No. 5,939,594 discloses the preparation of a superalkalinized  
7 alkylaryl sulfonate of alkaline earth metal. The alkyl group of the alkylaryl  
8 sulfonate contains between 14 to 40 carbon atoms and the aryl sulfonate  
9 radical of alkaline earth metal is fixed in a molar proportion comprised  
10 between 0 and 13% in positions 1 or 2 of the linear alkyl chain.

11 U.S. Pat. No. 6,031,144 discloses a process for reducing the residual olefin  
12 content of an alkylation reaction product by removing at least a portion of the  
13 non-alkylated single-ring aromatic hydrocarbon and then reacting the  
14 remaining alkylation reaction product in the presence of an acidic catalyst  
15 such as a molecular sieve or clay.

16 U.S. Pat. No. 6,337,310 discloses the preparation of alkylbenzene from  
17 preisomerized normal alpha olefins for making low overbased and high  
18 overbased sulfonates having a TBN in the range of 3 to 500. The process  
19 uses HF as catalyst or a solid acidic alkylation catalyst, such as a zeolite  
20 having an average pore size of at least 6 angstroms.

21 U.S. Pat. No. 6,525,234 discloses a process for alkylating aromatic using a  
22 porous crystalline material, e.g., MCM-22 and in situ regenerating the catalyst  
23 by use of a polar compound having a dipole moment of at least 0.05 Debyes.

24 It is known that most solid acid catalysts produce high 2-aryl attachment when  
25 alkylating with alpha-olefins. See S. Sivasanker, A. Thangaraj, "Distribution of  
26 Isomers in the Alkylation of Benzene with Long-Chain Olefins over Solid Acid



1 Catalysts," *Journal of Catalysis*, 138, 386-390 (1992). This is especially true  
2 for mordenite zeolite.

3 Two general treatises on zeolite are: Handbook of Molecular Sieves by  
4 Rosemarie Szostak (Van Nostrand Reinhold, New York 1992) and Molecular  
5 Sieves: Principles of Synthesis and Identification, 2<sup>nd</sup> Edition, by Rosemarie  
6 Szostak (Chapman and Hall, London, UK 1999).

## 7 SUMMARY OF THE INVENTION

8 The present invention is directed to novel alkylated aromatic compositions  
9 and processes for preparation of carbonated, overbased alkylated aromatic  
10 sulfonates, which processes comprise the alkylation in the presence of the  
11 catalyst composites of this invention, and further sulfonation and carbonation,  
12 overbasing of the alkylated aromatic sulfonic acids.

13 The present invention is also directed to zeolite catalyst compositions having  
14 a controlled macropore structure comprising zeolite Y and mordenite zeolite.

15 The present invention is also directed to a process for preparing the catalyst  
16 compositions. The catalysts and catalyst compositions exhibits reduced  
17 deactivation rates during the alkylation process, thereby increasing the life of  
18 the catalysts and the catalyst compositions.

19 In particular, the present invention is directed to an alkylated aromatic  
20 composition comprising a mixture of:

- 21 (a) an alkylated aromatic hydrocarbon alkylation product wherein the  
22 alkylation reaction is conducted in the presence of an alkylation  
23 catalyst having a macropore structure comprising zeolite Y, and  
24 wherein the peak macropore diameter of the catalyst, measured  
25 by ASTM Test No. D 4284-03, is less than or equal to about  
26 2000 angstroms and the cumulative pore volume of the catalyst

1 at pore diameters less than or equal to about 500 angstroms,  
2 measured by ASTM Test No. D 4284-03, is less than or equal to  
3 about 0.30 milliliters per gram; and

4  
5 (b) an alkylated aromatic hydrocarbon alkylation product wherein the  
6 alkylation reaction is conducted in the presence of an alkylation  
7 catalyst having a macropore structure comprising mordenite  
8 zeolite having a silica to alumina molar ratio of about 50 to about  
9 105 and wherein the peak macropore diameter of the catalyst,  
10 measured by ASTM Test No. D 4284-03, is less than or equal to  
11 about 900 angstroms and the cumulative pore volume of the  
12 catalyst at pore diameters less than or equal to about 500  
13 angstroms, measured by ASTM Test No. D 4284-03, is less than  
14 or equal to about 0.30 milliliters per gram.

15  
16 The weight percent of the alkylated aromatic hydrocarbon of (a) in the mixture  
17 may be in the range of about 40 percent to about 99 percent based on the  
18 total alkylated aromatic composition. Preferably the weight percent of the  
19 alkylated aromatic hydrocarbon of (a) in the mixture is in the range of about  
20 50 percent to about 90 percent based on the total alkylated aromatic  
21 composition, and more preferably the weight percent of the alkylated aromatic  
22 hydrocarbon of (a) in the mixture is in the range of about 70 percent to about  
23 80 percent based on the total alkylated aromatic composition.

24  
25 The alkyl groups of the alkylated aromatic composition may be derived from  
26 alpha olefins, isomerized olefins, branched-chain olefins, or mixtures thereof.  
27 The alpha olefins or the isomerized olefins have from about 6 carbon atoms to  
28 about 40 carbon atoms. Preferably, the alpha olefins or the isomerized olefins  
29 have from about 20 carbon atoms to about 40 carbon atoms. The branched-  
30 chain olefins have from about 6 carbon atoms to about 70 carbon atoms.  
31 Preferably, the branched-chain olefins have from about 8 carbon atoms to

1 about 50 carbon atoms. More preferably, the branched-chain olefins have  
2 from about 12 carbon atoms to about 18 carbon atoms.

3

4 The alkyl groups of the alkylated aromatic composition may be partially-  
5 branched-chain isomerized olefins wherein the olefins have from about  
6 6 carbon atoms to about 40 carbon atoms. Preferably, the partially-branched-  
7 chain isomerized olefins have from about 20 carbon atoms to about 40 carbon  
8 atoms.

9

10 The aromatic hydrocarbon of the alkylated aromatic composition may be  
11 benzene, toluene, xylene, cumene, or mixtures thereof. Preferably, the  
12 aromatic hydrocarbon is toluene or benzene.

13

14 The zeolite Y in step (a) and the mordenite zeolite in step (b) may contain a  
15 binder. Preferably, the binder in the zeolite Y in step (a) and the binder in the  
16 mordenite zeolite in step (b) is alumina.

17

18 The zeolite Y in step (a) and the mordenite zeolite in step (b) may be in the  
19 form of a tablet.

20

21 Another embodiment of the present invention is directed to a process for  
22 preparing an alkylated aromatic composition comprising:

23

24 (a) contacting at least one aromatic hydrocarbon with at least one  
25 olefin under alkylation conditions in the presence of a zeolite  
26 catalyst having a macropore structure comprising zeolite Y, and  
27 wherein the peak macropore diameter of the catalyst, measured by  
28 ASTM Test No. D 4284-03, is less than or equal to about  
29 2000 angstroms and the cumulative pore volume of the catalyst at  
30 pore diameters less than or equal to about 500 angstroms,  
31 measured by ASTM Test No. D 4284-03, is less than or equal to

1           about 0.30 milliliters per gram to form a first alkylated aromatic  
2           hydrocarbon product;

3

4           (b)   contacting at least one aromatic hydrocarbon with at least one  
5           olefin under alkylation conditions in the presence of a zeolite  
6           catalyst having a macropore structure comprising mordenite zeolite  
7           having a silica to alumina molar ratio of about 50 to about 105, and  
8           wherein the peak macropore diameter of the catalyst, measured by  
9           ASTM Test No. D 4284-03, is less than or equal to about  
10          900 angstroms and the cumulative pore volume of the catalyst at  
11          pore diameters less than or equal to about 500 angstroms,  
12          measured by ASTM Test No. D 4284-03, is less than or equal to  
13          about 0.30 milliliters per gram to form a second alkylated aromatic  
14          hydrocarbon product; and

15

16          (c)   combining the first alkylated aromatic hydrocarbon product and the  
17          second alkylated aromatic hydrocarbon product to form the  
18          alkylated aromatic composition;

19

20   wherein steps (a) and (b) can be conducted in any order.

21

22   The above process may further comprise in step (b) the reactivation of the  
23   deactivated zeolite catalyst with a suitable solvent flush, preferably the solvent  
24   is an aromatic hydrocarbon. More preferably, the aromatic hydrocarbon is  
25   benzene.

26

27   The above process may further comprise sulfonating the alkylated aromatic  
28   composition to form an alkylated aromatic sulfonic acid. The alkylated  
29   aromatic sulfonic acid may be reacted with an alkaline earth metal and carbon  
30   dioxide to produce a carbonated, overbased alkylated aromatic sulfonate.

31

1 The first alkylated aromatic hydrocarbon product in the alkylated aromatic  
2 composition may be in the range of about 40 percent to about 99 percent  
3 based on the total alkylated aromatic composition. Preferably, the first  
4 alkylated aromatic hydrocarbon product in the alkylated aromatic composition  
5 is in the range of about 50 percent to about 90 percent based on the total  
6 alkylated aromatic composition. More preferably, the first alkylated aromatic  
7 hydrocarbon product in the alkylated aromatic composition is in the range of  
8 about 70 percent to about 80 percent based on the total alkylated aromatic  
9 composition.

10

11 The olefin in step (a) and step (b) may be independently an alpha olefin, an  
12 isomerized olefin, a branched-chain olefin, or mixtures thereof. The alpha  
13 olefin or isomerized olefin may have from about 6 carbon atoms to about  
14 40 carbon atoms. Preferably, the alpha olefin or isomerized olefin has from  
15 about 20 carbon atoms to about 40 carbon atoms. The branched-chain olefin  
16 may have from about 6 carbon atoms to about 70 carbon atoms. Preferably,  
17 the branched-chain olefin has from about 8 carbon atoms to about 50 carbon  
18 atoms. More preferably, the branched-chain olefin has from about 12 carbon  
19 atoms to about 18 carbon atoms.

20

21 The olefin in step (a) or step (b) may be independently a partially-branched-  
22 chain isomerized olefin, and the olefin may have from about 6 carbon atoms  
23 to about 40 carbon atoms. Preferably, the partially-branched-chain  
24 isomerized olefin has from about 20 carbon atoms to about 40 carbon atoms.

25

26 The aromatic hydrocarbon of the alkylated aromatic composition may be  
27 benzene, toluene, xylene, cumene, or mixtures thereof. Preferably, the  
28 aromatic hydrocarbon is toluene or benzene.

29

30 The cumulative pore volume of the zeolite catalyst at pore diameters less than  
31 or equal to about 400 angstroms in step (a) and step (b) is less than or equal  
32 to about 0.30 milliliters per gram. Preferably, cumulative pore volume of the

1 zeolite catalysts at pore diameters less than or equal to about 300 angstroms  
2 in steps (a) and (b) is less than about 0.25 milliliters per gram, more  
3 preferably at pore diameters less than or equal to about 300 angstroms is less  
4 than about 0.20 milliliters per gram, and most preferably at pore diameters  
5 less than or equal to about 300 angstroms is in the range of about  
6 0.08 milliliters per gram to about 0.16 milliliters per gram.

7 The cumulative pore volume of the zeolite catalysts at pore diameters less  
8 than or equal to about 400 angstroms in steps (a) and (b) is in the range of  
9 about 0.05 milliliters per gram to about 0.18 milliliters per gram. Preferably,  
10 the cumulative pore volume of the zeolite catalysts at pore diameters less  
11 than or equal to about 300 angstroms in steps (a) and (b) is in the range of  
12 about 0.08 milliliters per gram to about 0.16 milliliters per gram.

13

14 The zeolite Y catalyst in step (a) has a peak macropore diameter in the range  
15 of about 700 angstroms to about 1800 angstroms. Preferably, the peak  
16 macropore diameter of the zeolite Y catalyst in step (a) is in the range of  
17 about 750 angstroms to about 1600 angstroms. More preferably, the peak  
18 macropore diameter of the zeolite Y catalyst in step (a) is in the range of  
19 about 900 angstroms to about 1400 angstroms.

20

21 In step (b), the peak macropore diameter of the mordenite zeolite catalyst is in  
22 the range of about 400 angstroms to about 800 angstroms. Preferably in  
23 step (b), the peak macropore diameter of the mordenite zeolite catalyst is in  
24 the range of about 400 angstroms to about 700 angstroms. More preferably  
25 in step (b), the peak macropore diameter of the mordenite zeolite catalyst is in  
26 the range of about 450 angstroms to about 600 angstroms.

27

28 In steps (a) in the above process, the zeolite Y catalyst has a silica to alumina  
29 ratio of about 5:1 to about 100:1. Preferably in step (a), the zeolite Y catalyst  
30 has a silica to alumina ratio of about 30:1 to about 90:1. More preferably in

1 step (a), the zeolite Y catalyst has a silica to alumina ratio of about 60:1 to  
2 about 80:1.

3

4 In step (b) in the above process, preferably the mordenite zeolite catalyst has  
5 a silica to alumina ratio of about 60:1 to about 80:1.

6

7 The zeolite Y in step (a) and the mordenite zeolite in step (b) may contain a  
8 binder. Preferably, the binder in the zeolite Y in step (a) and the binder in the  
9 mordenite zeolite in step (b) is alumina.

10

11 The zeolite Y in step (a) and the mordenite zeolite in step (b) may be in the  
12 form of a tablet.

13

14 A further embodiment of the present invention is directed to a process for  
15 preparing an alkylated aromatic composition comprising contacting at least  
16 one aromatic hydrocarbon with at least one olefin in the presence of a zeolite  
17 catalyst having a macropore structure comprising zeolite Y and mordenite  
18 zeolite having a silica to alumina ratio of about 50:1 to about 105:1, and  
19 wherein the peak macropore diameter of the catalyst, measured by ASTM  
20 Test No. D 4284-03, is less than or equal to about 2000 angstroms and the  
21 cumulative pore volume of the catalyst at pore diameters less than or equal to  
22 about 500 angstroms, measured by ASTM Test No. D 4284-03, is less than or  
23 equal to about 0.30 milliliters per gram.

24

25 The cumulative pore volume of the zeolite catalyst at pore diameters less than  
26 or equal to about 400 angstroms is less than or equal to about 0.30 milliliters  
27 per gram. Preferably, the cumulative pore volume zeolite catalyst at pore  
28 diameters less than or equal to about 300 angstroms is less than or equal to  
29 about 0.25 milliliters per gram. More preferably, the cumulative pore volume  
30 zeolite catalyst at pore diameters less than or equal to about 300 angstroms is  
31 less than or equal to about 0.20 milliliters per gram.

32

1 The cumulative pore volume of the zeolite catalyst at pore diameters less than  
2 or equal to about 400 angstroms may be in the range of about 0.05 milliliters  
3 per gram to about 0.18 milliliters per gram. Preferably, the cumulative pore  
4 volume of the zeolite catalyst at pore diameters less than or equal to about  
5 300 angstroms is in the range of about 0.08 milliliters per gram to about  
6 0.16 milliliters per gram.

7

8 The peak macropore diameter of the zeolite catalyst is in the range of about  
9 400 angstroms to about 1500 angstroms. Preferably, the peak macropore  
10 diameter of the zeolite catalyst is in the range of about 500 angstroms to  
11 about 1300 angstroms. More preferably the peak macropore diameter of the  
12 zeolite catalyst is in the range of about 600 angstroms to about  
13 1100 angstroms, and most preferably the peak macropore diameter of the  
14 zeolite catalyst is in the range of about 750 angstroms to about  
15 900 angstroms.

16

17 The zeolite Y has a silica to alumina molar ratio of about 5:1 to about 100:1  
18 and the mordenite zeolite has a silica to alumina molar ratio of about 50:1 to  
19 about 105:1. Preferably the zeolite Y has a silica to alumina molar ratio of  
20 about 30:1 to about 90:1, and more preferably the zeolite Y and the mordenite  
21 zeolite independently has a silica to alumina molar ratio of about 60:1 to about  
22 80:1.

23

24 The zeolite catalyst may contain a binder. Preferably, the binder is alumina.

25

26 The zeolite catalyst may be in the form of a tablet.

27

28 Yet another embodiment of the present invention is directed to a zeolite  
29 catalyst composition having a macropore structure comprising:

30

31 (a) zeolite Y; and

32



1 (b) mordenite zeolite having a silica to alumina molar ratio in the  
2 range of about 50:1 to about 105:1;

3  
4 wherein the peak macropore diameter of the catalyst composition, measured  
5 by ASTM Test No. D 4284-03, is less than about 2000 angstroms and the  
6 cumulative pore volume of the catalyst at pore diameters less than or equal to  
7 about 500 angstroms, measured by ASTM Test No. D 4284-03, is less than or  
8 equal to about 0.30 milliliters per gram.

9  
10 The cumulative pore volume of the zeolite catalyst composition at pore  
11 diameters less than or equal to about 400 angstroms is less than or equal to  
12 about 0.30 milliliters per gram. Preferably, the cumulative pore volume zeolite  
13 catalyst composition at pore diameters less than or equal to about  
14 300 angstroms is less than or equal to about 0.25 milliliters per gram. More  
15 preferably, the cumulative pore volume zeolite catalyst composition at pore  
16 diameters less than or equal to about 300 angstroms is less than or equal to  
17 about 0.20 milliliters per gram.

18  
19 The cumulative pore volume of the zeolite catalyst composition at pore  
20 diameters less than or equal to about 400 angstroms may be in the range of  
21 about 0.05 milliliters per gram to about 0.18 milliliters per gram. Preferably,  
22 the cumulative pore volume of the zeolite catalyst composition at pore  
23 diameters less than or equal to about 300 angstroms is in the range of about  
24 0.08 milliliters per gram to about 0.16 milliliters per gram.

25  
26 The peak macropore diameter of the zeolite catalyst composition is in the  
27 range of about 400 angstroms to about 1500 angstroms. Preferably, the peak  
28 macropore diameter of the zeolite catalyst composition is in the range of  
29 about 500 angstroms to about 1300 angstroms. More preferably the peak  
30 macropore diameter of the zeolite catalyst composition is in the range of  
31 about 600 angstroms to about 1100 angstroms, and most preferably the peak

1 macropore diameter of the zeolite catalyst composition is in the range of  
2 about 750 angstroms to about 900 angstroms.

3

4 The zeolite Y in step (a) having a silica to alumina ratio of about 5:1 to about  
5 100:1, preferably the zeolite Y has a silica to alumina molar ratio of about 30:1  
6 to about 90:1, and more preferably the zeolite Y has a silica to alumina molar  
7 ratio of about 60:1 to about 80:1.

8

9 The mordenite zeolite in step (b) preferably has a silica to alumina molar ratio  
10 of about 60:1 to about 80:1.

11

12 The zeolite catalyst composition may contain a binder. Preferably, the binder  
13 is alumina.

14

15 The zeolite catalyst composition may be in the form of a tablet.

16

## 17 DETAILED DESCRIPTION OF THE INVENTION

18

### DEFINITIONS

19 The term "alkylate" means an alkylated aromatic hydrocarbon.

20 The term "2-aryl content" is defined as the percentage of total alkylate (the  
21 alkylate species in which the alkyl chain derived from the olefin employed in  
22 the present alkylation process is attached to the aromatic ring) that is  
23 comprised of those chemical species in which the attachment of the alkyl  
24 chain to the aromatic ring is at the 2-position along the alkyl chain.

25 The term "binder" means any suitable inorganic material which can serve as  
26 matrix or porous matrix to bind the zeolite particles into a more useful shape.

1 The term “branched-chain olefins” means olefins derived from the  
2 polymerization of olefin monomers higher than ethylene and containing a  
3 substantial number of branches wherein the branches are alkyl groups having  
4 from about one carbon atom to about 30 carbon atoms. Mixtures of ethylene  
5 and higher olefins are also contemplated.

6 The term “calcining” as used herein means heating the catalyst to about  
7 400°C to about 1000°C in a substantially dry environment.

8 The term “carbonated, overbased” is used to describe those alkaline earth  
9 metal alkyl aromatic sulfonates in which the ratio of the number of equivalents  
10 of the alkaline earth metal moiety to the number of equivalents of the aromatic  
11 sulfonic acid moiety is greater than one, and is usually greater than 10 and  
12 may be as high as 20 or greater.

13 The term “cumulative pore volume” obtained by Mercury Intrusion Porosimetry  
14 as used herein refers to that part of the total volume in milliliters per gram  
15 derived from the graphical, cumulative pore volume distribution, measured by  
16 Section 14.1.6 of ASTM D 4284-03, or the corresponding tabular presentation  
17 of the same data between defined upper and lower pore diameters. When no  
18 lower diameter limit is defined, the lower limit is the lowest detection limit or  
19 lowest radius measured by Section 14.1.6 of ASTM D 4284-03.

20 The terms “dry basis”, “anhydrous basis”, and “volatiles-free basis” shall refer  
21 to the dry weight of catalyst composite or raw materials expressed on a metal  
22 oxides basis such as  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$ .

23 The term “flush” as used herein means contacting the deactivated mordenite  
24 catalysts and mordenite catalyst composites of this invention in the reactor  
25 with a suitable solvent, such as an aromatic hydrocarbon for reactivation of  
26 the mordenite catalysts and mordenite catalyst composites.

1 The term “loss-on-ignition (LOI)” as used herein means the percent weight  
2 loss of the zeolite composite and raw material samples which volatilize or  
3 evaporate when heated to 538°C for 1 hour. When the temperature is greater  
4 than or equal about 538°C, the “loss-on-ignition” approximates the percent  
5 volatiles.

6 The terms “macropore”, “mesopore”, and “micropore” as used herein follow  
7 the definitions set forth by the International Union of Pure and Applied  
8 Chemistry (IUPAC), Division of Physical Chemistry, in Manual of Symbols and  
9 Terminology for Physicochemical Quantities and Units, Appendix II  
10 Definitions, Terminology and Symbols in Colloid and Surface Chemistry Part I,  
11 Adopted by the IUPAC Council at Washington, D. C., USA, on 23 July, 1971.  
12 Pores with widths or diameters exceeding ~50 nanometers (500 angstroms)  
13 are called “macropores”. Pores with widths or diameters not exceeding  
14 ~2.0 nanometers (20 angstroms) are called “micropores”. Pores of  
15 intermediate size (2.0 nanometers < width or diameter ≤ 50 nm) are called  
16 “mesopores”.

17 The term “Mercury Intrusion Porosimetry” refers to the ASTM Test  
18 No. D 4284–03 used to determine pore volume distribution of catalysts by  
19 Mercury Intrusion Porosimetry. Mercury pore distribution was measured  
20 using a Quantachrome Scanning Mercury Porosimeter Model SP-100. The  
21 software version used by the instrument is V2.11 (dated 10/27/93). Surface  
22 tension used in the calculation is 473 dynes per centimeter and the contact  
23 angle is 140 degrees.

24 The terms “normal alpha olefin” and “linear alpha olefin” mean those  
25 straight-chain olefins without a significant degree of alkyl branching in which  
26 the carbon to carbon double bond resides primarily at the end or “alpha”  
27 position of the carbon chain, i.e., between C<sub>1</sub> and C<sub>2</sub>. Normal alpha olefins  
28 are derived from polymerization of ethylene.

1 The term "normal alpha olefin isomerization" means the conversion of normal  
2 alpha olefins into isomerized olefins having a lower alpha olefin content (the  
3 double bond is between C<sub>1</sub> and C<sub>2</sub>), higher internal olefin content (the double  
4 bond is in positions other than between C<sub>1</sub> and C<sub>2</sub>), and optionally a higher  
5 degree of branching.

6 The term "partially-branched chain olefin" is defined as the olefin product of  
7 isomerization of normal alpha olefins wherein the degree of branching is  
8 higher than in the starting normal alpha olefins.

9 The term "peak macropore diameter" as used herein means the peak  
10 diameter (i.e., the diameter within the macropore region at which the  
11 differential plot of pore size distribution, as defined by Section 14.2, reaches a  
12 maximum) in the macropore range determined by ASTM Test No. 4284-03 for  
13 the macropore peak in the catalysts of the present invention.

14 The term "peptizing" means the dispersion of large aggregates of binder  
15 particles, including hydrated aluminas, into much smaller primary particles by  
16 the addition of acid.

17 The term "percent volatiles" as used herein means the difference between the  
18 actual weight of the catalyst composite or the raw materials and the weight of  
19 the material on a dry, anhydrous, or volatiles-free basis, expressed as a  
20 percentage of the actual sample weight.

21 The term "SAR" or "silica to alumina ratio" refers to the molar ratio of silicon  
22 oxide to aluminum oxide; mol SiO<sub>2</sub>:mol AlO<sub>3</sub>.

23 The term "sufficient water to shape the catalyst material" means quantity of  
24 water required to make an acid peptized mixture of zeolite and alumina  
25 powders into an extrudable mass.

1 The term "tableting" as used herein refers to the process of forming a catalyst  
2 aggregate from zeolite powder or a mixture of zeolite and binder powders by  
3 compressing the powder in a die.

4 The term "total pore volume" obtained by Mercury Intrusion Porosimetry as  
5 used herein refers to the total pore volume in milliliters per gram derived from  
6 the graphical, cumulative pore volume distribution (Section 14.1.6 of ASTM  
7 D 4284-03) or the corresponding tabular presentation of the same data.

8 As used herein, all percentages are weight percent, unless otherwise  
9 specified.

10 As noted above, the present invention is directed to novel alkylated aromatic  
11 compositions and their sulfonated and carbonated products. The alkylation of  
12 the aromatic hydrocarbons is carried out in the presence of the zeolite catalyst  
13 compositions of the present invention having a controlled macropore structure  
14 comprising zeolite Y and mordenite zeolite. The catalysts of the present  
15 invention were characterized by pore volume distribution obtained by Mercury  
16 Intrusion Porosimetry, ASTM Test No. D 4284-03. Mercury Intrusion  
17 Porosimetry provides a graph of cumulative pore volume (pv) versus pore  
18 diameter (pd). Mercury Intrusion Porosimetry also is used to determine the  
19 macropore peak diameter from the derivative, delta pv ( $\Delta pv$ ) divided by delta  
20 pd ( $\Delta pd$ ). The graphs are used to characterize the catalysts of the present  
21 invention.

22 The zeolite catalyst compositions were prepared using zeolite Y and  
23 mordenite zeolite. Zeolite Y and mordenite zeolite may also be combined to  
24 prepare zeolite catalyst compositions of the present invention. When the  
25 zeolite catalyst compositions contain both zeolite Y and mordenite zeolite, the  
26 zeolite catalyst composite may be prepared by mixing zeolite Y and mordenite  
27 zeolite powders before the binding and shaping steps. The zeolite Y  
28 CBV 760® and CBV 600® available from Zeolyst International having a

1 nominal silica to alumina ratio of 60 and 6.7, respectively, may be used for  
2 preparing the zeolite catalyst compositions of this invention. However,  
3 zeolite Y having a silica to alumina ratio between 5 and 110 may be used for  
4 the preparation of the zeolite catalysts compositions of the present invention.  
5 The mordenite zeolite 90A® having a nominal silica to alumina ratio of 90,  
6 also available from Zeolyst International, may be used for preparing the  
7 zeolite catalyst compositions of this invention. Mordenite zeolite having a  
8 silica to alumina ratio of 50 to 105 may be used in the preparation of the  
9 zeolite catalyst compositions of this invention.

10 The catalysts of the present invention may be shaped or formed into tablets,  
11 extrudates or any other shape using procedures well known in the prior art.  
12 The preparation of extrudates requires the presence of a binder, such as  
13 alumina. The tabletted catalysts do not require the presence of a binder, but  
14 a binder may be present in a tabletted zeolite catalyst. The crystalline zeolite  
15 powder may be compressed to form a tablet. The tabletted catalysts of the  
16 present invention provide exceptionally low deactivation rates in alkylation  
17 reactions.

18 The alkylation of aromatic hydrocarbons with one or more olefins may be  
19 carried out in a fixed bed reactor in the presence of the zeolite catalysts  
20 compositions of the present invention comprising only zeolite Y, only  
21 mordenite zeolite, or both zeolite Y and mordenite zeolite. The alkylation  
22 process is conducted without the addition of water and using dried aromatic  
23 hydrocarbon and olefin feed. It is believed that the presence of water during  
24 the alkylation increases the deactivation rate of the catalysts of this invention.  
25 When the alkylation using zeolite Y and mordenite zeolite is carried out in  
26 separate fixed bed reactors, the alkylated aromatic hydrocarbons may be  
27 combined to obtain the desired amount of alpha olefins versus branched-  
28 chain olefins. Alkylation reactions using normal alpha olefins and zeolite  
29 catalysts compositions comprising only mordenite zeolite give predominantly  
30 alkylated aromatic hydrocarbons wherein the attachment of the of the alkyl

1 chain to the aromatic ring is at the 2-position along the alkyl chain. On the  
2 other hand, alkylation reactions using zeolite catalysts compositions  
3 comprising only zeolite Y and normal alpha olefins give predominantly  
4 attachments at other than the 2-position along the alkyl chain.

5 The alkylation reaction may be carried out by any conventionally known  
6 process. The aromatic hydrocarbon is reacted with one or more olefins in the  
7 presence of a catalyst of the present invention under alkylation reaction  
8 conditions. The above alkylation process is conducted without the addition of  
9 water and using dried aromatic hydrocarbon and olefin feed. It is believed  
10 that the presence of water during the alkylation process increases the  
11 deactivation rate of the catalysts of this invention.

12 The aromatic hydrocarbon may be single-ring or double-ring, preferably the  
13 aromatic hydrocarbon is a single-ring aromatic hydrocarbon. The aromatic  
14 hydrocarbon may be an alkylated aromatic hydrocarbon, such as a  
15 mono-alkylated aromatic hydrocarbon, wherein the alkyl group has from about  
16 4 carbon atoms to about 80 carbon atoms. When the aromatic hydrocarbon  
17 used is a mono-alkylated aromatic, the product of the alkylation reaction is a  
18 di-alkylated aromatic hydrocarbon.

19 The olefins useful for alkylation of the aromatic hydrocarbons may be  
20 linear-chain olefins or branched-chain olefins having from about 4 carbon  
21 atoms to about 80 carbon atoms. In addition, normal alpha olefins may be  
22 isomerized to obtain partially-branched-chain olefins for use in alkylation  
23 process of the present invention. These resulting partially-branched-chain  
24 olefins may be alpha-olefins, beta-olefins, internal-olefins, tri-substituted  
25 olefins, and vinylidene olefins.

26 Alkylated aromatic hydrocarbon sulfonic acids of the alkylated aromatic  
27 hydrocarbons of the present invention may be prepared by any known  
28 sulfonation reaction. The alkylated aromatic sulfonic acids may be further



1 reacted with an alkaline earth metal and carbon dioxide to obtain carbonated,  
2 overbased alkylated aromatic sulfonates useful as detergents in lubricating  
3 oils. Carbonation may be carried out by any conventionally known process.  
4 The degree of overbasing may be controlled by changing the reaction  
5 conditions and the amount of the alkaline earth metal and carbon dioxide  
6 used in the carbonation process.

7 The novel alkylation compositions of the present invention may be obtained  
8 by conducting the alkylation reactions as described above in the presence of  
9 the zeolite catalyst compositions of the present invention prepared as  
10 described in Examples 1-4 below.

#### 11 Procedure for Isomerization of Normal Alpha Olefins

12 The isomerization process may be carried out in batch or continuous mode.  
13 The process temperatures can range from 50°C to 250°C. In the batch mode,  
14 a typical method is to use a stirred autoclave or glass flask, which may be  
15 heated to the desired reaction temperature. A continuous process is most  
16 efficiently carried out in a fixed bed process. Space rates in a fixed bed  
17 process can range from 0.1 to 10 or more weight hourly space velocity.

18 In a fixed bed process, the isomerization catalyst is charged to the reactor and  
19 activated or dried at a temperature of at least 150°C under vacuum or flowing  
20 inert, dry gas. After activation, the temperature of the isomerization catalyst is  
21 adjusted to the desired reaction temperature and a flow of the olefin is  
22 introduced into the reactor. The reactor effluent containing the partially-  
23 branched, isomerized olefins is collected. The resulting partially-branched,  
24 isomerized olefins contain a different olefin distribution (alpha olefin, beta  
25 olefin, internal olefin, tri-substituted olefin, and vinylidene olefin) and  
26 branching content than the unisomerized olefin.

1    Procedure for Alkylation of Aromatic Hydrocarbons

2    Alkylation of aromatic hydrocarbons with normal alpha olefins, partially-  
3    branched-chain isomerized olefins, and branched-chain olefins may be carried  
4    out by any method known by a person skilled in the art.

5    The alkylation reaction is typically carried out with an aromatic hydrocarbon  
6    and an olefin in molar ratios from 1:15 to 25:1. Process temperatures can  
7    range from about 100°C to about 250°C. The process is carried out without  
8    the addition of water. As the olefins have a high boiling point, the process is  
9    preferably carried out in the liquid phase. The alkylation process may be  
10    carried out in batch or continuous mode. In the batch mode, a typical method  
11    is to use a stirred autoclave or glass flask, which may be heated to the  
12    desired reaction temperature. A continuous process is most efficiently carried  
13    out in a fixed bed process. Space rates in a fixed bed process can range from  
14    0.01 to 10 or more weight hourly space velocity.

15    In a fixed bed process, the alkylation catalyst is charged to the reactor and  
16    activated or dried at a temperature of at least 150°C under vacuum or flowing  
17    inert, dry gas. After activation, the alkylation catalyst is cooled to ambient  
18    temperature and a flow of the aromatic hydrocarbon compound is introduced,  
19    optionally toluene. Pressure is increased by means of a back pressure valve  
20    so that the pressure is above the bubble point pressure of the aromatic  
21    hydrocarbon feed composition at the desired reaction temperature. After  
22    pressurizing the system to the desired pressure, the temperature is increased  
23    to the desired reaction temperature. A flow of the olefin is then mixed with the  
24    aromatic hydrocarbon and allowed to flow over the catalyst. The reactor  
25    effluent comprising alkylated aromatic hydrocarbon, unreacted olefin and  
26    excess aromatic hydrocarbon compound are collected. The excess aromatic  
27    hydrocarbon compound is then removed by distillation, stripping, evaporation  
28    under vacuum, or any other means known to those skilled in the art.

1    Procedure for Sulfonation of Alkylated Aromatic Hydrocarbons

2    Sulfonation of alkylated hydrocarbons may be carried out by any method  
3    known by a person skilled in the art.

4    The sulfonation reaction is typically carried out in a falling film tubular reactor  
5    maintained at about 65°C. The alkylated aromatic hydrocarbon is placed in  
6    the tube and sulfur trioxide diluted with nitrogen is added to the alkylated  
7    aromatic hydrocarbon. The molar ratio of alkylated aromatic hydrocarbon to  
8    sulfur trioxide is maintained at about 1.05:1. The resulting alkylated aromatic  
9    sulfonic acid may be diluted with about 10% 100 Neutral oil followed by  
10   thermal treatment with nitrogen bubbling at a rate of about 10 liters per  
11   kilogram of product and stirring while maintaining the temperature at about  
12   85°C until the desired residual sulfuric acid content is obtained (maximum of  
13   about 0.5%).

14   Procedure for Carbonation, Overbasing of Alkylated Aromatic Sulfonic Acids

15   Carbonation, overbasing of alkylaromatic sulfonic acids may be carried out by  
16   any method known by a person skilled in the art to produce alkylaromatic  
17   sulfonates.

18  
19   Generally, the carbonation, overbasing reaction is carried out in a reactor in  
20   the presence of the alkylated aromatic sulfonic acid, diluent oil, an aromatic  
21   solvent, and an alcohol. The reaction mixture is agitated and alkaline earth  
22   metal and carbon dioxide are added to the reaction while maintaining the  
23   temperature between about 20°C and 80°C.

24  
25   The degree of carbonation, overbasing may be controlled by the quantity of  
26   the alkaline earth metal and carbon dioxide added to the reaction mixture, the  
27   reactants and the reaction conditions used during the carbonation process.

## 1    Reactivation of Deactivated Mordenite Zeolite Catalysts and Composites

2    Once the mordenite zeolite catalysts and catalyst composites are completely  
3    deactivated, the alkylation reaction stops because of the polymerization of the  
4    olefin into large molecular species that cannot diffuse out of the crystal  
5    micropores containing the active sites in the zeolitic material. However,  
6    reactor bed need not be changed to remove the deactivated mordenite zeolite  
7    catalysts and catalyst composites. The deactivated mordenite zeolite  
8    catalysts and catalyst composites are reactivated at the end of an alkylation  
9    run by stopping the olefin feed stream to the reactor and permitting the  
10    aromatic hydrocarbon stream to continue to be flushed through the reactor for  
11    a sufficient time, typically from about 12 hours to about 24 hours.

## 12                                    EXAMPLES

### 13                                    Example 1

#### 14                                    Preparation of Zeolite Catalyst Composition 1

15    Zeolite Catalyst Composition 1 is prepared by mixing zeolite Y powder and  
16    mordenite zeolite powder available from Zeolyst International or any other  
17    commercial source. The zeolite Y and mordenite zeolite powders are mixed  
18    in any proportion based on the desired alkylated aromatic product.

19    As an example, zeolite Y catalyst powder is mixed with mordenite zeolite  
20    catalyst powder to obtain a final ratio of 85:15 in the final Zeolite Catalyst  
21    Composition.

22    Zeolite Catalyst Composition 1 is prepared by the following method:

23    Loss-on-ignition (LOI) is determined for samples of commercially available  
24    zeolite Y (CBV 760® and CBV 600®) and mordenite zeolite (CBV 90A®)  
25    available from Zeolyst International by heating the samples to 538°C for  
26    1 hour. The LOI obtained provides the percent volatiles in the zeolite Y and

1 mordenite zeolite batches being used. The LOI of a commercial sample of  
2 Versal® hydrated aluminum oxide available from Sasol is also obtained by  
3 heating the samples to 538°C for 1 hour. Next, based on the results obtained  
4 from the LOI of the zeolite Y, mordenite zeolite and the alumina powders the  
5 amount of alumina powder is weighed out to obtain 80% (volatile-free basis)  
6 zeolite content of the composite consists of 85% zeolite Y and 15% mordenite  
7 zeolite on a volatile-free basis.

8 The three dry powders are added to a Baker Perkins mixer and dry mixed for  
9 4 minutes. The amount of concentrated (70.7%) nitric acid to give  
10 0.7 weight % (based on 100% nitric acid) of the dry weight of the zeolite and  
11 the alumina powders is calculated. This amount of 70.7% nitric acid was  
12 weighed out and dissolved in deionized water.

13 The total amount of water and 70.7% nitric acid needed to obtain a final  
14 concentration of approximately 50% total volatiles is calculated as follows.  
15 Volatiles in the Y zeolite, mordenite zeolite and alumina powders is  
16 calculated. Nitric acid solution is considered to be 100% volatiles. Thus, the  
17 amount of deionized water that must be added is the difference between the  
18 final concentration of volatiles of 50% minus the total volatiles in the three  
19 powders.

20 Deionized water is added over a period of 5 minutes to the powders in the  
21 mixer using a peristaltic pump. The mixer is then stopped so that the walls of  
22 the mixer can be scraped down. Mixing is then resumed and the solution of  
23 nitric acid in water is added over 5 minutes using the peristaltic pump. At the  
24 end of acid addition, mixing is continued for a total time of 40 minutes, with  
25 occasional holds to allow for scraping the sides of the mixer. At the end of the  
26 mixing period, the percent volatiles are measured. Additional amounts of  
27 deionized water is added until the mixture appears extrudable and the percent  
28 volatiles are again measured.

1 The wet mixture is extruded through 1.27 millimeters, asymmetric quadrilobe  
2 die inserts, in a Bonnot extruder. The wet long cylindrical strands are dried at  
3 121°C for 8 hours. The long cylindrical strands are then broken to give  
4 extrudates with length to diameter ratio of 2:6. The extrudates are sieved and  
5 the portion larger than 1.0 millimeter is retained.

6 The extrudates are then calcined in a muffle furnace using the following  
7 temperature program:

8 The extrudates are heated to 593°C over two hours, then held at 593°C for  
9 1/2 hour and next cooled to 204°C. A total weight of the extrudates is  
10 obtained.

11 Mercury Intrusion Porosimetry is used to characterize the extrudates. A peak  
12 macropore diameter in angstroms and a cumulative pore volume at diameters  
13 less than 300 angstroms is obtained from the Mercury Intrusion Porosimetry  
14 data.

15 The Zeolite Catalyst Composition is charged to a pilot plant reactor used for  
16 the alkylation of aromatic hydrocarbons. The reaction effluent of this reactor  
17 has greater than or equal to 99% conversion of the olefin feed stream. When  
18 benzene is used as the aromatic hydrocarbon and the alkylation reaction is  
19 conducted using the Zeolite Catalyst Composition, there is a much higher  
20 attachment of the alkyl chain to the aromatic ring at the 2-position along the  
21 alkyl chain in the alkylated benzene than when the zeolite Y catalyst  
22 composite is used alone in the alkylation reaction.

23 Excess benzene is removed by distillation, stripping or any other suitable  
24 means and the alkylated benzene is sulfonated using sulfonation procedures  
25 well known in the art. The alkyl benzene sulfonic acid is further carbonated  
26 with an alkaline earth metal and carbon dioxide.

1 Example 2

2 Preparation of Zeolite Y Catalyst Composite

3 Zeolite Y Catalyst Composite was prepared are described above in  
4 Example 1 using zeolite Y CBV 760® available from Zeolyst International.

5 Example 3

6 Preparation of Mordenite Zeolite Catalyst Composite

7 Mordenite Zeolite Catalyst Composite was prepared are described above in  
8 Example 1 using mordenite zeolite CBV 90A® available from Zeolyst  
9 International.

10 Example 4

11 Preparation of Zeolite Catalyst Composition 2

12 Zeolite Catalyst Composition 2 is prepared by mixing Zeolite Y Catalyst  
13 Composite and Mordenite Zeolite Catalyst Composite prepared in Examples 2  
14 and 3. The Zeolite Y Catalyst Composite and Mordenite Zeolite Catalyst  
15 Composite are mixed in any proportion based on the desired alkylated  
16 aromatic product. As an example, Zeolite Y Catalyst Composite is mixed with  
17 Mordenite Zeolite Catalyst Composite to obtain a final ratio of 85:15 in the  
18 Zeolite Catalyst Composition 2.

19 The resulting Zeolite Catalyst Composition 2 is charged to a pilot plant reactor  
20 for the alkylation of aromatic hydrocarbons as described below in Example 5.

21 Example 5

22 Preparation of alkylbenzene compositions using zeolite Y catalyst composite

23 Typically, alkylation of aromatic hydrocarbons with normal alpha olefins,  
24 partially-branched-chain isomerized olefins and branched-chain olefins was  
25 carried out as described below:

1 A fixed bed reactor constructed from 15.54 millimeters Schedule 160 stainless  
2 steel pipe was used for this alkylation test. Pressure in the reactor was  
3 maintained by an appropriate back pressure valve. The reactor and heaters  
4 were constructed so that adiabatic temperature control could be maintained  
5 during the course of alkylation runs. A 192 gram bed of 850 micrometer to  
6 2 millimeters Alundum particles was packed in the bottom of the reactor to  
7 provide a pre-heat zone. Next, 100 grams of a zeolite Y catalyst composite  
8 similar to the zeolite Y catalyst composite prepared in Example 2 above was  
9 charged to the fixed bed reactor. The reactor was gently vibrated during  
10 loading to give a maximum packed bulk density of catalyst in the reactor.  
11 Finally, void spaces in the catalyst bed were filled with 351 grams  
12 150 micrometers Alundum particles as interstitial packing.  
13  
14 The reactor was then closed, sealed, and pressure tested under nitrogen.  
15 Next, the alkylation catalyst was dehydrated during 15 hours at 200°C under a  
16 20 liters per hour flow of nitrogen measured at ambient temperature and  
17 pressure and then cooled to 100°C under nitrogen. Benzene was then  
18 introduced into the catalytic bed in an up-flow manner at a flow rate of  
19 195 grams per hour. Temperature (under adiabatic temperature control) was  
20 increased to a start-of-run temperature of 182°C (measured just before the  
21 catalyst bed) and the pressure was increased to 14.6 atmospheres.  
22  
23 When temperature and pressure had lined out at desired start-of-run  
24 conditions of 182°C and 14.6 atmospheres, a feed mixture, consisting of  
25 benzene and C<sub>20-24</sub> NAO at a molar ratio of 10:1 and dried over activated  
26 alumina, was introduced in an up-flow manner. As the feed reached the  
27 catalyst in the reactor, reaction began to occur and internal catalyst bed  
28 temperatures increased above the inlet temperature. After about 8 hours  
29 on-stream, the reactor exotherm was 20°C. At 26 hours on-stream, the olefin  
30 conversion in the product was 99.1%. The run was stopped after 408 hours  
31 on-stream, although the run could have continued. At this time, the olefin  
32 conversion was 99.45%.



1 Alkylated aromatic hydrocarbon products containing excess benzene were  
2 collected during the course of the run. After distillation to remove excess  
3 aromatic hydrocarbon, analysis showed that greater than 99% conversion of  
4 olefin was achieved during the course of the run.

5 A fixed bed reactor was constructed from 15.54 millimeters Schedule 160  
6 stainless steel pipe. Pressure in the reactor was maintained by an  
7 appropriate back pressure valve. The reactor and heaters were constructed  
8 so that adiabatic temperature control could be maintained during the course of  
9 alkylation runs. A small amount of 850 micrometer to 2 millimeters  
10 acid-washed Alundum was packed in the bottom of the reactor to provide a  
11 pre-heat zone. Next, 100 grams of whole alkylation extrudate catalyst was  
12 charged to the fixed bed reactor. Finally, void spaces in the catalyst bed were  
13 filled with 150 micrometers acid-washed Alundum interstitial packing. The  
14 zeolite Y or the mordenite zeolite alkylation catalyst was then dehydrated for  
15 at least 8 hours at 200°C under a flow of nitrogen gas and then cooled to  
16 ambient temperature under nitrogen gas. Benzene was then introduced into  
17 the catalytic bed in an up-flow manner. Temperature (isothermal temperature  
18 control) and pressure were increased at start of run conditions. Normal  
19 operating pressure was 11.91 atmospheres. The initial temperature of  
20 approximately 150°C was chosen so that the temperature in the catalytic bed  
21 increased under adiabatic temperature control to about 160°C to about 175°C.  
22 When temperature and pressure had lined out at desired start-of-run  
23 conditions, the reactor system was switched to adiabatic temperature control.  
24 A dried feed mixture, consisting of olefin and benzene, was introduced in an  
25 up-flow manner. The benzene to olefin molar ratio was 10:1. As the reaction  
26 began to occur, temperature increased in the catalyst bed above the inlet  
27 temperature.

28

29 Alkylated benzene product containing excess benzene was collected during  
30 the course of the run. After distillation to remove excess benzene, analysis  
31 showed that greater than 99% conversion of olefin was achieved during the  
32 course of the run.

## Example 6

### Preparation of alkylbenzene compositions

Typically, alkylation of aromatic hydrocarbons with normal alpha olefins, partially-branched-chain isomerized olefins and branched-chain olefins was carried out as described below:

A fixed bed reactor was constructed from 15.54 millimeters Schedule 160 stainless steel pipe. Pressure in the reactor was maintained by an appropriate back pressure valve. The reactor and heaters were constructed so that adiabatic temperature control could be maintained during the course of alkylation runs. A bed of 170 grams of 850 micrometer to 2 millimeters Alundum particles was packed in the bottom of the reactor to provide a pre-heat zone. Next, 100 grams of mordenite catalyst composite similar to the mordenite catalyst composite prepared in Example 3 above was charged to the fixed bed reactor. Finally, void spaces in the catalyst bed were filled with 309 grams of 150 micrometers Alundum particles interstitial packing. The reactor was gently vibrated while charging catalyst and alundum to ensure a high packed bulk density. After charging, the reactor was closed, sealed, and the pressure was tested.

The alkylation catalyst was then heated to 200°C under a 20 liters per hour flow of nitrogen measured at ambient temperature and pressure and dehydrated for 23 hours at 200°C. The catalyst bed was then cooled to 100°C under nitrogen. Benzene was then introduced into the catalytic bed in an up-flow manner at a flow rate of 200 grams per hour. Temperature (under adiabatic temperature control) was increased to a start of run inlet temperature of 154°C (measured just before the catalyst bed) and the pressure was increased to 12.66 atmospheres.

When temperature and pressure had lined out at desired start-of-run conditions of 154°C and 12.66 atmospheres, a feed mixture, consisting of

1 benzene and C<sub>20-24</sub> NAO at a molar ratio of 15:1 and dried over activated  
2 alumina, was introduced in an up-flow manner at 200 grams per hour. As the  
3 feed reached the catalyst in the reactor, reaction began to occur and internal  
4 catalyst bed temperatures increased above the inlet temperature. After about  
5 8 hours on-stream, the reactor exotherm was 20°C. In the first 57 hours  
6 on-stream, the olefin conversion decreased from 100% to 98.8% (Run  
7 Period 1). At this point, the catalyst bed was flushed with benzene at  
8 200 grams per hour during 18 hours. Following the benzene flush, the  
9 benzene and olefin feed flow was resumed. Inlet temperature was increased  
10 to 162°C at 57 run hours. Feed was continued until 351 run hours (Run  
11 Period 2 from 57 to 351 run hours). Olefin conversion was initially 98.9%  
12 during Run Period 2 but declined to 98.1% at 321 run hours and further to  
13 95.3% at 351 run hours. A second benzene flush was performed at 351 run  
14 hours during 17 hours. After the second benzene flush, feed flow was  
15 resumed again to start Run Period 3. Feed was continued until 550 run  
16 hours. Olefin conversion was initially 98.5% but declined to 98.3% at 519 run  
17 hours and to 97.0% at 550 run hours. A third benzene flush was done during  
18 a weekend. Feed flow was resumed after the third benzene flush to begin  
19 Run Period 4. At the beginning of Run Period 4, olefin conversion was 98.8%  
20 and at 942 run hours the olefin conversion was 98.4%. The run was stopped  
21 after 942 hours on-stream but could have continued longer.

22

23 Alkylated aromatic hydrocarbon products containing excess benzene were  
24 collected during the course of the run. After distillation to remove excess  
25 aromatic hydrocarbon, analysis showed that greater than 97% conversion of  
26 olefin was achieved during most of the course of the run.

27

28

#### Example 7

29

#### Preparation of alkylbenzene sulfonic acids

30 A mixture of 85 weight % of the alkylated benzene prepared using the  
31 zeolite Y catalyst and 15 weight % of the alkylated benzene prepared using

1 mordenite zeolite catalyst as in Examples 5 and 6 above was sulfonated by a  
2 concurrent stream of sulfur trioxide ( $\text{SO}_3$ ) and air with in a tubular reactor  
3 (2 meters long, 1 centimeter inside diameter) in a down flow mode using the  
4 following conditions:

5  
6 Reactor temperature was  $60^\circ\text{C}$ ,  $\text{SO}_3$  flow rate was 73 grams per hour, and  
7 alkylate flow rate was 327 grams per hour at a  $\text{SO}_3$  to alkylate molar ratio of  
8 1.05. The  $\text{SO}_3$  was generated by passing a mixture of oxygen and sulfur  
9 dioxide ( $\text{SO}_2$ ) through a catalytic furnace containing vanadium oxide ( $\text{V}_2\text{O}_5$ ).  
10

11 The resulting crude alkylbenzene sulfonic acid had the following properties  
12 based on the total weight of the product: weight % of  $\text{HSO}_3$  was 15.61 % and  
13 weight % of  $\text{H}_2\text{SO}_4$  was 0.53.  
14

15 The crude alkylbenzene sulfonic acid (1665 grams) was diluted with 83 grams  
16 of 100 Neutral diluent oil and placed in a 4 liter four-neck glass reactor fitted  
17 with a stainless steel mechanical agitator rotating at about 300 rpm, a  
18 condenser and a gas inlet tube (2 millimeters inside diameter) located just  
19 above the agitator blades for the introduction of nitrogen. The contents of the  
20 reactor were placed under vacuum (40 millimeters Hg) and the reactor was  
21 heated to  $110^\circ\text{C}$  with stirring and nitrogen was bubbled through the mixture at  
22 about 30 liters per hour for about 30 minutes until the weight % of  $\text{H}_2\text{SO}_4$  is  
23 less than about 0.3 weight %. This material is the final alkylbenzene sulfonic  
24 acid.  
25

26 The final alkylbenzene sulfonic acid had the following properties based on the  
27 total weight of the product: weight % of  $\text{HSO}_3$  was 14.95 and weight % of  
28  $\text{H}_2\text{SO}_4$  was 0.17.  
29

## Example 7

### Preparation of alkylbenzene sulfonates

To a 5 liter four-neck glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at between 300 and 350 rpm, a gas inlet tube (2 millimeters inside diameter) located just above the agitator blades for the addition of CO<sub>2</sub>, a distillation column and condenser under nitrogen gas was charged 129.4 grams of centrate.

The centrate was a mixture of the sludge fractions previously produced during the purification of high TBN carbonated, overbased synthetic sulfonates by centrifugation and decantation and was added to the reaction mixture of this example for recycling the contents of the centrate. The centrate had a TBN of 197 and contained approximately 73 grams of xylene solvent, 12 grams active calcium sulfonate, 9 grams calcium hydroxide and calcium carbonate, 8 grams of carbon dioxide, and 23 grams of 100 Neutral diluent oil.

Next, 40 grams of methanol, 207 grams of xylene solvent, 296.5 grams (0.59 mole) of the alkylbenzene sulfonic acid (HSO<sub>3</sub> was 14.95 weight % based on the total weight of the reaction mixture) from Example 6 above was charged to the reactor over 15 minutes at room temperature. A slurry of 160 grams (2.16 mole) of calcium hydroxide, 362 grams of xylene solvent and 94.2 grams of methanol was added to the reactor and the contents of the reactor were cooled to 25°C. Subsequently, 33 grams (0.79 mole) of CO<sub>2</sub> was added to the reactor through the gas inlet tube over 39 minutes while the temperature of the reactor increased to about 32°C. A second slurry composed of 160 grams (2.16 mole) of calcium hydroxide, 384 grams xylene solvent, and 131 grams of methanol was then added to the reactor concurrently with 0.9 grams of CO<sub>2</sub> over about 1 minute. Then 92 grams of CO<sub>2</sub> was added to the reactor over 64 minutes while the temperature of the reactor was increased from about 30°C to about 41°C. A third slurry

1 composed of 82 grams of oxide and 298 grams of xylene solvent was then  
2 charged to the reactor concurrently with 1.4 grams of CO<sub>2</sub> over about  
3 1 minute. Next, 55 grams (1.25 mole) of CO<sub>2</sub> was added to the reactor over  
4 approximately 60 minutes while keeping the reactor temperature at  
5 approximately 38°C.

6  
7 The water and methanol were then distilled from the reactor by first heating  
8 the reactor to 65°C over about 40 minutes at atmospheric pressure and then  
9 to 93°C over about 60 minutes at atmospheric pressure and then finally to  
10 130°C over about 30 minutes at atmospheric pressure. The temperature of  
11 the reactor was then decreased to 110°C over about 60 minutes at  
12 atmospheric pressure and next then cooled to approximately 30°C and  
13 475.7 grams of 600 Neutral diluent oil was added to the reactor followed by  
14 413 grams of xylene solvent. The sediment in the product was then removed  
15 by centrifugation. The xylene solvent in the product was distilled by heating  
16 the product to 204°C over approximately 45 minutes at 30 millimeters Hg  
17 vacuum and holding the product at 204°C and 30 millimeters Hg vacuum for  
18 10 minutes. The vacuum was replaced with nitrogen gas and the contents  
19 allowed to cool to room temperature to obtain the overbased sulfonate having  
20 the following properties based on the total weight of the product:

21  
22 The weight % of calcium was 16.2, TBN was 429, weight % of sulfur was  
23 1.70, weight % of calcium sulfonate was 0.94, and viscosity was 111 cSt at  
24 100°C.